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**JAPANESE / ENGLISH TRANSLATION OF
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Method for Producing Polyester Raw Material**

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(54) [Title of the Invention]

Method for Producing Polyester Raw Material

(57) [Summary]

[Object] An object of the present invention is to provide a method for producing a polyester raw material comprising terephthalic acid and an alkylene glycol with small capital investment and small energy consumption, and a method for improving the slurry properties of the alkylene glycol and terephthalic acid produced by means of a DMT hydrolysis reaction.

[Means of Achievement] A large amount of energy required for a drier, and a drying step can be dispensed with as a result of substituting an alkylene glycol for a terephthalic acid/water slurry

obtained from the terephthalic acid production step, without drying the slurry. The handling properties of the terephthalic acid/alkylene glycol slurry produced by means of a DMT hydrolysis may further be improved as the result of forming a slurry of the alkylene glycol with terephthalic acid that is allowed to retain a small amount of water without being dried.

[Claims]

[Claim 1] A method for producing polyester raw material, characterized by means of obtaining a mixture of terephthalic acid and water in the production of terephthalic acid, and thereafter substituting an alkylene glycol, which is a raw material for a polyester polycondensation reaction in which terephthalic acid is used, for water in this mixture.

[Claim 2] The method for producing polyester raw material cited in claim 1, wherein the production of terephthalic acid is performed with a method based on the hydrolysis of dimethyl terephthalate (DMT) and/or monomethyl terephthalate (MMT).

[Claim 3] The method for producing polyester raw material cited in either claim 1 or 2, wherein the production of terephthalic acid is performed with a method based on liquid-phase oxidation of paraxylene (PX).

[Claim 4] The method for producing polyester raw material cited in any of claims 1 to 3, wherein water is removed from the water-containing alkylene glycol used for substitution, and the alkylene glycol is thereafter reused as a substitute.

[Claim 5] The method for producing polyester raw material cited in any of claims 1 to 3, wherein water is removed from the water-containing alkylene glycol used for substitution, and the alkylene glycol is thereafter reused as a raw material in other steps.

[Claim 6] The method for producing polyester raw material cited in any of claims 1 to 3, wherein terephthalic acid and water are subjected to solid-liquid separation prior to substituting with an alkylene glycol.

[Claim 7] Polyester raw material obtained by means of the method cited in any of claims 1 to 3, wherein the molar ratio between alkylene glycol and terephthalic acid in the polyester raw material is 1:0.1 to 10.

[Claim 8] Polyester raw material obtained by means of the method cited in any of claims 1 to 3, wherein the water content of the polyester raw material is 0.1 to 20% by weight with respect to alkylene glycol.

[Claim 9] Polyester raw material obtained by means of the method cited in any of claims 1 to 3, wherein the water content of the polyester raw material is 1 to 5% by weight with respect to alkylene glycol.

[Claim 10] The polyester raw material cited in any of claims 7 to 9, wherein the alkylene glycol is ethylene glycol.

[Claim 11] The polyester raw material cited in any of claims 7 to 10, wherein the polyester is polyethylene terephthalate (PET).

[Claim 12] The polyester raw material cited in any of claims 7 to 11, wherein the polyester raw material is for use in polyethylene terephthalate (PET) packaging material.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a method for producing raw material for polyester products that are widely used in fibers, films, industrial components, packaging materials, common molded articles, and the like, and more particularly to a method for separating terephthalic acid from liquid comprising principally water to obtain a cake comprising principally terephthalic acid, and for producing polyester raw material comprising a terephthalic acid/alkylene glycol mixture as a result of substituting an alkylene glycol (which is a principal component of polyester) for water in the cake.

[0002]

[Prior Art] A method whereby paraxylene (PX) is oxidized in a liquid phase with molecular oxygen, and a method whereby dimethyl terephthalate (DMT) is hydrolyzed (DE-1618503, JP (Kokai) 55-141433, and other publications) are well-known methods for industrially producing terephthalic acid.

[0003] Typical PX liquid-phase oxidation is performed by means of feeding molecular oxygen gas (normally air) and subjecting PX to liquid-phase oxidation in the presence of a catalyst containing a bromine compound and a compound of cobalt, manganese, or another transition metal in a low aliphatic carboxylic acid, for example, an acetic acid solvent. Because the resulting terephthalic acid has poor solubility in an acetic acid solvent, it is precipitated to form a terephthalic acid slurry. The terephthalic acid in this terephthalic acid slurry normally contains a considerable amount of impurities, so further refinement is required. A typical example of a

refinement method is to separate coarse terephthalic acid crystals obtained in the liquid-phase oxidation of PX from the acetic acid solvent, to form this into an aqueous medium (normally a water slurry), to thereafter heat-dissolve the system, and to pass the system through a reaction bed filled with a noble metal catalyst together with hydrogen gas under a high temperature and high pressure to obtain an aqueous solution of refined terephthalic acid. This aqueous solution is gradually cooled in a plurality of crystallization tanks, the terephthalic acid dissolved in the solvent is precipitated, and the system is subjected to solid-liquid separation and dried to obtain a terephthalic acid product.

[0004] A typical method of DMT hydrolysis is to obtain DMT from PX by means of a well-known technique, to refine the DMT as a result of distillation or another means to obtain highly refined DMT, and to thereafter hydrolyze the refined DMT under a high temperature and high pressure to obtain an aqueous solution of terephthalic acid. The aqueous solution is cooled, thereafter subjected to solid-liquid separation, and dried and crushed to obtain a terephthalic acid product. Both methods have drawbacks in that the system must be formed into a dried powder for storage and transport, a drying step for completely eliminating water with considerable latent heat of vaporization is required, and higher capital investment and a very large amount of energy during operation are required.

[0005] When terephthalic acid is used as a raw material for polyester, a mixture with an alkylene glycol (which is a principal component) is produced if the polyester is polyethylene terephthalate (a typical example of polyester), and the mixture is esterified and then polymerized. It is known that at this time when a large amount of water is intermixed, the esterification reaction is inhibited and the speed of the reaction is decreased. It is also known that terephthalic acid produced by means of PX liquid-phase oxidation forms individual spherical particles, and but terephthalic acid produced as a result of a DMT hydrolysis forms an aggregate. Because of this aggregate structure, the slurry must be formed with an alkylene glycol when fed to the polymerization step, but the terephthalic acid produced by means of DMT hydrolysis requires a greater amount of alkylene glycol than in the case of PX liquid-phase oxidation. A drawback exists in that a byproduct diethylene glycol (DEG) is produced (when the alkylene glycol is ethylene glycol) when an excessive amount of alkylene glycol is added in the polymerization step, and the hue of the polymer consequently worsens.

[0006]

[Problems to Be Solved by the Invention] A first object of the present invention is related to a method for producing terephthalic acid that is fed to the polyester production step, and is to provide a method for producing polyester raw material with small energy consumption without the need for a drying step and/or a drying and crushing step. A second object of the present invention is related to a method for producing terephthalic acid in a DMT hydrolysis reaction, and is to provide a method for forming a slurry with the same amount of alkylene glycol as that used to obtain terephthalic acid by means of PX liquid-phase oxidation.

[0007]

[Means Used to Solve the Above-Mentioned Problems] The objects of the present invention are achieved by means of subjecting a terephthalic acid/water slurry to solid-liquid separation to obtain a cake, and substituting an alkylene glycol (which is a raw material for polymerization) for the water in the cake.

[0008]

[Embodiments of the Invention] The production method of the present invention may adopt either PX liquid-phase oxidation or DMT hydrolysis without any drawback for the production of terephthalic acid, but DMT hydrolysis is particularly advantageous. The terephthalic acid/water slurry that is formed as a result of the reaction or other action is subjected to continuous solid-liquid separation, and the cake is added to the substitution tank. When the solid-liquid separator is operating steadily, the moisture content in the cake can be held substantially constant, and the moisture content at the current technological level is about 10 to 30%.

[0009] The filtrate comprises principally water due to filtrate leakage and yields a liquid mixture containing terephthalic acid. The liquid mixture may be reused as reaction water in DMT hydrolysis, and as recrystallization solvent in PX liquid-phase oxidation. The required amount of alkylene glycol for substitution is calculated from the operating condition of the solid-liquid separator in the substitution tank, and is continuously added. The amount of alkylene glycol added at this time is 4 to 999 times by weight with respect to the amount of water that accompanies the cake, but is preferably 18 to 99 times by weight. The amount of water contained in the alkylene glycol may be adjusted by the amount of alkylene glycol at this stage. It should be noted that ethylene glycol is preferable as the alkylene glycol. In other words, the

objective polyester is preferably polyethylene terephthalate in the present invention. After the system is sufficiently agitated in the substitution tank, a cake that accompanies alkylene glycol and principally comprises terephthalic acid can be obtained by means of subjecting the system to solid-liquid separation again. The cake is sent to the slurry adjustment tank, and alkylene glycol is added at this point so as to achieve a suitable molar ratio of terephthalic acid/alkylene glycol (1:0.1 to 10) while adjusting the consistency of the slurry.

[0010] It should be noted that after water is removed from the water-containing alkylene glycol that was used for substitution, the alkylene glycol may be reused for substitution. Furthermore, after water is removed from the water-containing alkylene glycol that was used for substitution, the alkylene glycol may be reused as a raw material in other steps.

[0011] It is known that the structure of the particles of terephthalic acid obtained by means of DMT hydrolysis and PX liquid-phase oxidation are different in that those of the former are an aggregate while those of the latter are independent particles. The handling properties of the terephthalic acid/alkylene glycol slurry are considerably affected by the presence of water in the slurry, and the effect of water being contained therein is advantageous for terephthalic acid that is produced by means of DMT hydrolysis in particular. The amount of water contained in the polyester raw material comprising the terephthalic acid/alkylene glycol mixture that is obtained in such a manner should have a weight ratio of 0.1 to 20 wt% with respect to the alkylene glycol, but is preferably about 1 to 5 wt%. Achieving a moisture content of 0.1 wt% or less is operationally difficult, and if the moisture content exceeds 20 wt% the esterification reaction is inhibited and the reaction speed is reduced when the system is fed to the esterification step and to the subsequent polymerization step.

[0012] The polyester raw material obtained by means of the present invention may be used in mostly all applications of polyester, and is advantageously used in polyester films, polyethylene terephthalate (PET) packaging materials, and other applications that particularly require a high purity of raw material.

[0013]

[Working Examples] The essence of the present invention is explained in detail below with working examples, but the present invention is not limited in any manner by these.

Working Example 1

Terephthalic acid was synthesized by means of DMT hydrolysis under reaction conditions of 250°C for three hours. After the reaction, the terephthalic acid was separated with the help of filtration from the resulting mixture of reaction mother liquor and terephthalic acid to obtain a wet cake. The moisture content of the wet cake was measured by means of sampling a portion of the wet cake and determining the change in weight from before drying to after drying. The amount of ethylene glycol (EG) for substitution that was added to the cake on that basis was calculated, and a cake was obtained after further filtration. Polyester raw material was then prepared by adjusting the terephthalic acid/EG ratio. The moisture content in the EG was measured with a Karl Fisher moisture meter. When the particle size of the terephthalic acid obtained under the above-described conditions was measured with a wet sieving method, the mean particle size was found to be 150 µm. The results of working example 1 are shown in Table 1.

[0014]

[Table 1]

Moisture content [wt%]	Terephthalic acid/EG ratio [mol/mol]					
	1.0	1.25	1.5	1.75	2.0	20
0.001	×	×	×	×	×	○
0.2	×	×	×	▲	○	○
1.0	×	▲	◎	◎	◎	○
10.0	×	▲	◎	○	○	○
50.0	▲	○	△	△	△	△
PET hue	-	Good	Good	Good	Good	Poor (yellow)

[0015]

×: Blocks form without any fluidity

▲: Becomes a slurry, but the slurry viscosity is high and fluidity is poor

△: Becomes a slurry, but the slurry stability is poor and the particles quickly precipitate

○: Slurry properties and stability are both good

◎: Slurry properties and stability are both very good

[0016] Working Example 2

Terephthalic acid was synthesized by means of PX liquid-phase oxidation. After the reaction, the terephthalic acid was separated with the help of filtration from the resulting mixture

of reaction mother liquor and terephthalic acid to obtain a wet cake. The moisture content of the wet cake was measured by means of sampling a portion of the wet cake and determining the change in weight from before drying to after drying. The amount of ethylene glycol (EG) for substitution that was added to the cake on that basis was calculated, and a cake was obtained after further filtration. Polyester raw material was then prepared by adjusting the terephthalic acid/EG ratio. The moisture content in the EG was measured with a Karl Fisher moisture meter. When the particle size of the terephthalic acid obtained under the above-described conditions was measured with a wet sieving method, the mean particle size was found to be 118 μm . The results of working example 2 are shown in Table 2.

[0017]

[Table 2]

Moisture content [wt%]	Terephthalic acid/EG ratio [mol/mol]					
	1.0	1.25	1.5	1.75	2.0	20
0.001	×	×	◎	◎	○	○
0.2	×	×	◎	○	○	○
1.0	×	×	○	○	○	○
10.0	×	▲	○	○	△	△
50.0	▲	○	△	△	△	△
PET hue	-	Good	Good	Good	Good	Poor (yellow)

[0018]

×: Blocks form without any fluidity

▲: Becomes a slurry, but the slurry viscosity is high and fluidity is poor

△: Becomes a slurry, but the slurry stability is poor and the particles quickly precipitate

○: Slurry properties and stability are both good

◎: Slurry properties and stability are both very good

[0019] Comparative Example 1

Terephthalic acid was synthesized by means of DMT hydrolysis under reaction conditions of 250°C for three hours. After the reaction, the terephthalic acid was separated with the help of filtration from the resulting mixture of reaction mother liquor and terephthalic acid to obtain a wet cake. The mother liquor was then completely removed with a dryer. The EG was added to the dried terephthalic acid to form a slurry, and a cake was thereafter obtained with the help of filtration. Polyester raw material was then prepared by means of adjusting the

terephthalic acid/EG ratio. When the particle size of the terephthalic acid obtained under the above-described conditions was measured with a wet sieving method, the mean particle size was found to be 150 µm. The results of comparative example 1 are shown in Table 3.

[0020]

[Table 3]

Moisture content [wt%]	Terephthalic acid/EG ratio [mol/mol]					
	1.0	1.25	1.5	1.75	2.0	20
0	✗	✗	✗	✗	✗	○
PET hue	-	-	-	-	-	Poor (yellow)

[0021]

✗: Blocks form without any fluidity

▲: Becomes a slurry, but the slurry viscosity is high and fluidity is poor

△: Becomes a slurry, but the slurry stability is poor and the particles quickly precipitate

○: Slurry properties and stability are both good

◎: Slurry properties and stability are both very good

[0022] Comparative Example 2

Terephthalic acid was synthesized by means of PX liquid-phase oxidation. After the reaction, the terephthalic acid was separated with the help of filtration from the resulting mixture of reaction mother liquor and terephthalic acid to obtain a wet cake. The mother liquor was then completely removed with a dryer. The EG was added to the dried terephthalic acid to form a slurry, and a cake was thereafter obtained with the help of filtration. Polyester raw material was then prepared by means of adjusting the terephthalic acid/EG ratio. When the particle size of the terephthalic acid obtained under the above-described conditions was measured with a wet sieving method, the mean particle size was found to be 118 µm. The results of working example 2 are shown in Table 4.

[0023]

[Table 4]

Moisture content [wt%]	Terephthalic acid/EG ratio [mol/mol]					
	1.0	1.25	1.5	1.75	2.0	20
0	✗	✗	✗	○	○	○
PET hue	-	-	-	Good	Good	Poor (yellow)

[0024]

✗: Blocks form without any fluidity

▲: Becomes a slurry, but the slurry viscosity is high and fluidity is poor

△: Becomes a slurry, but the slurry stability is poor and the particles quickly precipitate

○: Slurry properties and stability are both good

◎: Slurry properties and stability are both very good

[0025] Comparative Example 3

Terephthalic acid was synthesized by means of DMT hydrolysis under reaction conditions of 250°C for three hours. After the reaction, the terephthalic acid was separated with the help of filtration from the resulting mixture of reaction mother liquor and terephthalic acid to obtain a wet cake. The mother liquor was then completely removed with a dryer. The EG was added to the dried terephthalic acid to form a slurry, and a cake was thereafter obtained with the help of filtration. The terephthalic acid/EG ratio was adjusted, and polyester raw material was thereafter prepared by means of adding water so that the moisture content of the EG was brought to a prescribed concentration. When the particle size of the terephthalic acid obtained under the above-described conditions was measured with a wet sieving method, the mean particle size was found to be 150 µm. The results of comparative example 3 are shown in Table 5.

[0026]

[Table 5]

Moisture content [wt%]	Terephthalic acid/EG ratio [mol/mol]					
	1.0	1.25	1.5	1.75	2.0	20
0.001	✗	✗	✗	✗	▲	◎
0.2	✗	✗	✗	✗	▲	○
1.0	✗	✗	▲	▲	○	○
10.0	✗	▲	▲	○	○	○
50.0	▲	▲	○	△	△	△
PET hue	-	Good	Good	Good	Good	Poor (yellow)

[0027]

✗: Blocks form without any fluidity

▲: Becomes a slurry, but the slurry viscosity is high and fluidity is poor

△: Becomes a slurry, but the slurry stability is poor and the particles quickly precipitate

○: Slurry properties and stability are both good

◎: Slurry properties and stability are both very good

[0028]

[Effect of the Invention] According to the present invention, raw material suitable for the production of polyester can be produced without consuming of a large amount of energy in a drying step. In the manufacturing method for terephthalic acid that uses DMT hydrolysis in particular, the slurry properties can be improved while keeping the terephthalic acid/alkylene glycol ratio at the same level sought in conventional polyester raw material, and can contribute to stable production.

(Continued from front page)

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